Compressed arsenolite $\text{As}_4\text{O}_6$ and its helium clathrate $\text{As}_4\text{O}_6\cdot2\text{He}$

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Crystal structure of arsenolite, the cubic polymorph of arsenic(III) oxide, has been determined by single crystal X-ray diffraction up to 30 GPa. The bulk of the crystal is monotonically compressed with no detectable anomalies, to 60% of the initial volume at 30 GPa. In the structure the most compressed are $\text{As}^\cdots\text{As}$ contacts which contrasts with increased intramolecular $\text{As}^\cdots\text{As}$ distance in the deformed molecule. The ratio between $\text{As}^\cdots\text{As}$ inter- and intramolecular distances decreases from 1.47 at 0.1 MPa to 1.03 at 30 GPa. The $\text{AsO}_6$ molecules are deformed to become more tetrahedron-like. Pressure above 3 GPa favours the formation of $\text{AsO}_6\cdot2\text{He}$ inclusion compound in the surface layer increasingly deeper with pressure. The experimental $\text{As}_4\text{O}_6$ crystal compression has been compared with various theoretical models within the DFT framework. According to band-structure calculations the arsenolite band gap falls from 4.2 eV at ambient pressure to 2.7 eV at 27.8 GPa.

Introduction

Arsenolite is a well-known mineral till recently generally used for various industrial, agricultural, chemical and household applications owing to its strong toxicity and exceptional properties. Polymorphism of arsenic(III) oxide has attracted attention for years. There are two minerals of $\text{As}_2\text{O}_3$ – cubic arsenolite containing adamantane-like $\text{As}_4\text{O}_6$ molecules packed in a 3D diamond network $^{1,2}$ and monoclinic claudetite I consisting of highly corrugated $\text{As}_2\text{O}_3$ layers $^{3-5}$. In the late 1940s another monoclinic modification was discovered and called claudetite II due to its extended $\text{As}_2\text{O}_3$ layers resembling those of of claudetite I. $^{6,7}$ Well-known is also a glassy $\text{As}_2\text{O}_3$ modification. There are a few reports on the studies of arsenic(III) oxide polymorphs under high pressure. The arsenolite-claudetite I equilibrium as a function of temperature and pressure was studied extensively in the 1960s. It was suggested that arsenolite undergoes a reversible transition to claudetite I at 110$\pm$10°C when subjected to shear stress. $^8$ In another high-pressure (HP) study of arsenolite, claudetite I and glassy $\text{As}_2\text{O}_3$, Soignard et al. compressed arsenolite in non-hydrostatic conditions up to 35 GPa and observed its amorphisation above 20 GPa. $^9$ Grzechik’s Raman and IR spectroscopy study of arsenolite up to 16 GPa suggested a phase transition at 6 GPa, lowering the cubic symmetry to tetragonal and retaining two molecules per the primitive unit cell. He also noted that hydrostatic or quasi-hydrostatic pressure, as opposed to shear stress, does not induce arsenolite-claudetite I transition. $^{10}$ However, no structural information about the HP arsenolite and its compressibility was measured. Presently we report this information determined by synchrotron single-crystal X-ray diffraction up to 30 GPa and theoretically modelled by DFT calculations. They reveal considerable structural transformations reducing the molecular character of the crystal, supported by DFT band structure and density of states for arsenolite at ambient pressure and around 30 GPa. We also found a pressure-induced solvation of arsenolite with helium above 3 GPa.

Results and discussion

Crystal structure and diffraction pattern

At ambient pressure arsenolite is a typical molecular crystal. It is built of adamantanoid $\text{As}_4\text{O}_6$ molecules (Fig. 1) located at highly symmetric 4$\bar{3}$m sites of cubic space group $Fd\bar{3}m$. The bulk of the crystal is monotonically compressed in the whole pressure range of our study. No anomalies have been detected to 30 GPa either in the lattice parameters (Fig. 2) or in the intermolecular distances and molecular dimensions (Figs. 3 and 4). This indicates that previously observed anomalies at 6 GPa in the Raman and IR spectra of mixed arsenolite and CsI powders $^{10}$ were caused by the non-hydrostatic effects in the sample, rather than any phase transition in arsenolite. In our study He environment ensured perfectly hydrostatic conditions to 11.6 GPa, and pseudohydrostatic conditions above, $^{11}$ whereas CsI is harder than arsenolite even at normal conditions. Pressure induces systematic distortions of the molecular geometry (Figs. 3 and 4). Although no changes in the $\text{As}^\cdots\text{O}$ bond length can be noted within experimental error, $\text{As}^\cdots\text{As}$ and $\text{O}^\cdots\text{As}$ bond angles are bent in the opposite sense and consequently, the intermolecular distances $\text{As}^\cdots\text{As}$ increase and $\text{O}^\cdots\text{O}$ decrease (Fig. 3). These changes, of about 2% of the ambient-pressure values, are much smaller than the compression of intermolecular contacts. Oxygen atoms are pushed towards $\text{As}^\cdots\text{As}$ intramolecular edges which are elongated as pressure increases and the molecule becomes more tetrahedron-like. This is most likely the result of the $\text{O}^\cdots\text{O}$ packing interactions which have already been found to be very important in the understanding of silicate structures under...
The intermolecular As—O distances are all well below the level of As and O van der Waals radii sum (3.37 Å) and they fall steadily upon pressure increase. The As—As separation in the tetrahedral (As$_4$O$_6$)$_4$ clusters decreases from 4.6090(5) Å at 0.1 MPa to 3.4268(7) Å at 30 Gpa, passing the doubled As van der Waals radius (3.70 Å) at 15 Gpa. The As—As distance at 30 Gpa equals 74% of that at ambient pressure, while the analogous ratio for the As—O contact at 30 Gpa is 79%, indicating that the compression of tetrahedral clusters is slightly more significant than the compression of As$_4$O$_6$ dimers (see Fig. 1b,c).

Fig. 1 (a) Molecular structure of arsenolite with As$_4$ tetrahedron marked in green; (b) (As$_4$O$_6$)$_2$ dimer with As—O separations marked with dashed brown lines; (c) (As$_4$O$_6$)$_4$ cluster with As—As intermolecular distances marked with light blue dashed lines.

Fig. 2 EoS curves for experimental and theoretical (p,V/Z) data. Filled and empty black circles denote experimental data corresponding to compression and decompression, respectively.

Fig. 3 As—O bond length, intramolecular As—As separation as well as intermolecular As—O and As—As distances plotted as a function of pressure for both experimental and theoretical data.

Fig. 4 O—As—O and As—O—As bond angles plotted as a function of pressure for both experimental and theoretical data.
Starting from 3.28(9) GPa additional weak “ghost” reflections appear on the lower 2θ-angle side of the main reflections of the AsO₆ sample (see Figs. 5a and S1). The intensity of most of these “ghost” reflections increases with pressure, reaching 10-15% of the main reflections at the 29.83(5) GPa limit of our data (see Fig. S2). The “ghost” reflections can be indexed according to the face-centered cubic lattice with the parameter aₕ being about 2% longer than that of the main AsO₆ crystal. This ratio is somewhat smaller for the series of measurements with the compressed sample than for the decompression run (Fig. 5b and Table S5). After eliminating possibilities of instrumental artefacts, of spurious radiation or multiple diffraction as the origin of the “ghost” reflections, they have been associated with the formation of AsO₂·He inclusion compound promoted by pressure higher than 3.28(9) GPa.

This compound is formed on the surface of arsenolite sample and the He-permeation depth increases with pressure, as indicated by the intensity of “ghost” reflections. The formation and decomposition of the AsO₂·He clathrate have been supported by a small hysteresis of “ghost”-lattice unit-cell volume upon sample compression and decompression (Fig. 5b). The diffusion of “ghost” reflections can be due to the strain between the crystal bulk and the helium-permeated surface. When assuming the helium atom position in the largest voids, located at 0, 0, 0 (Fig. 6), an improved fit between observed and calculated structure factors has been obtained. Although the precise read-out of the intensity of “ghost” reflections is hampered by their diffusion and proximity of many stronger main reflections, the simple structure of AsO₂·He allows the determination of intermolecular distances in this crystal. The closest As⋯He contact is 2.7456(18) Å at 7.71(8) GPa and 2.4517(14) Å at 29.83(5) GPa, whereas the closest O⋯He contacts are 2.698(11) Å and 2.444(4) Å, respectively. These distances are compatible with van der Waals radii of helium, arsenic and oxygen when taking into account their considerable compression in this pressure range. Further investigations in different pressure transmitting media are planned to verify the hypothesis.

Recently, a high-pressure structural study on senarmonite – cubic antimony(III) oxide has been carried out. It undergoes two isostructural phase transitions at 3.5 and 10 GPa consisting in adamantane-like SbO₆ molecules becoming 3D covalent network. Cubic symmetry has been retained during the transitions but significant changes in bulk modulus have occurred. Similar effects were not observed for arsenolite up to 30 GPa and this could be related to the fact that intermolecular contacts in senarmonite are shorter than in arsenolite at ambient pressure as evidenced by the Sb⋯O and As⋯O contacts of 2.9018(9) and 3.041(2) Å, respectively. Interestingly, the geometry of AsO₆ molecule under 20.07(9) GPa is very similar to that of SbO₆ at ambient pressure, as evidenced by the bond angles and bond valency values (see Table S6). This suggests that the crystal structure of senarmonite at a given pressure is very similar to that of arsenolite.
but under higher pressures. It could be concluded then that arsenolite should undergo isostructural transitions similar to that observed in senarmontite under pressures higher than 30 GPa.

Crystal structure – comparison between experiment and computations

We performed theoretical calculations of arsenolite crystal structure under pressure utilising various quantum mechanical models to compare their accuracy in the description of the system. We utilised density functional theory (DFT)\(^\text{16,17}\) with two various basis sets – plane waves and localised Gaussian type atomic orbitals in the form of pob-TZVP basis set\(^\text{18}\). Two functionals with dispersion corrections treated with the Grimme method were studied, namely PBE-D2 functional from the GGA family of functionals\(^\text{19,20}\) and the hybrid B3LYP-D\(*\) functional with the Grimme correction optimised for solid state calculations by Civa\textit{leri} et al\(^\text{21}\). A total of three models denoted PAW_PBE-D2, pob-TZVP_PBE-D2 and pob-TZVP_B3LYP-D\(*\) were tested. The PAW calculations performed with the VASP code were carried out as constant volume optimisations and the external pressure was the result of the volume constraint whereas the pob-TZVP computations, effected in the CRYSTAL09 suite, were executed as full geometry optimisations under external pressure defined in the input. Interestingly, all of the models overestimate the As–O bond lengths by ca. 0.03-0.05 Å (cf. Fig. 2). The discrepancies for As–O intermolecular distances are a little smaller and the PBE-D2 model has been found to perform better than the B3LYP-D\(*\). The agreement between experimental and calculated As–O–As and O–As–O bond angles is remarkable with most of the calculated values lying within one standard uncertainty (s.u.) from the experimental values.

Equation of state

Third order Birch-Murnaghan equation of state (EoS):\(^\text{22}\)

\[
p = \frac{3}{2} B_0 \left( \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right) \left[ 1 + \frac{3}{4} (B'_0 - 4) \left( \frac{V_0}{V} \right)^{\frac{4}{3}} - 1 \right]
\]

where \(V_0\) is volume at zero pressure, \(B_0\) bulks modulus and \(B'_0\) is bulk modulus first derivative with respect to pressure, has been fitted to the experimental as well as theoretical (\(p, V/Z\)) set of points using weights for both pressure and volume s.u.’s. \(Z\) is the number of As\textsubscript{6}O\textsubscript{6} molecules in the unit cell and consequently \(V/Z\) is molecular volume. The resulting EoS parameters are given in the Table 1 and the EoSs curves are plotted together with experimental and computed points in Fig. 2.

<table>
<thead>
<tr>
<th></th>
<th>(V_0/Z)/ Å(^3)</th>
<th>(B_0)/ GPa</th>
<th>(B'_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>168.7(6)</td>
<td>11.8(5)</td>
<td>8.6(2)</td>
</tr>
<tr>
<td>PAW_PBE-D2</td>
<td>169.1(4)</td>
<td>10.0(5)</td>
<td>10.5(4)</td>
</tr>
<tr>
<td>pob-TZVP_PBE-D2</td>
<td>162.8(14)</td>
<td>21(2)</td>
<td>7.0(5)</td>
</tr>
<tr>
<td>pob-TZVP_B3LYPD(*)</td>
<td>172.0(18)</td>
<td>18(2)</td>
<td>6.4(5)</td>
</tr>
</tbody>
</table>

\(^*\) \(V_0/Z\) is molecular volume at zero pressure

Agreement between the experimental and PAW_PBE-D2 data is extraordinary. It is noteworthy that these calculations were performed in the \(P1\) space group and the analysis of the optimised geometries indicates that they all exhibit the symmetry of the cubic \(Fd\overline{3}m\) space group which supports our experimental result that no lowering of symmetry occurs in arsenolite upon compression. Surprisingly, the agreement is worst for the pob-TZVP_B3LYP-D\(*\) model even though the B3LYP functional is used extensively for computations of molecules and the dispersion correction has been optimised for molecular crystals. The application of Gaussian basis set leads to significant overestimation of the bulk modulus and also to significant increase in its standard uncertainty.

Band structure

Band structure and density of states (DOS) in arsenolite crystal structures at 0.06 GPa (top) and at 27.8 GPa (bottom). Red and green lines denote As and O partial DOS, respectively. X stands for (0.5, 0.5, 0), \(\Gamma\) for (0, 0, 0) and \(\Lambda\) for (0.5, 0.5, 0.5) points in the reciprocal lattice.

Band structure

Band structure and density of states (DOS) have been computed to see if any interesting changes occur in the arsenolite’s electronic structure upon compression, given that As–As separations fall below the sum of As van der Waals radii as pressure increases (see Fig. 3). PAW method with plane wave basis set was utilised with PBE exchange-correlation functional and Grimme’s D2 correction for dispersion. Computations have shown that arsenolite is an insulator at 0.06 GPa with a band gap of 4.2 eV which drops to 2.7 eV making cubic As\textsubscript{6}O\textsubscript{6} semiconducting at 27.8 GPa (Fig. 7).
Electronic bands tend to be more diffuse at high pressure, but no significant changes in the As and O partial DOS relative to one another have occurred upon the pressure increase.

**Conclusions**

The arsenolite crystal structure in the pressure range from 0 to 30 GPa is compressed monotonically and no phase transitions have been detected. The crystal structure undergoes smooth compression and decompression without hysteresis in the studied pressure range. The As atoms are displaced toward outside of As=Os molecules with pressure and O atoms are simultaneously pushed inside which makes the molecule more tetrahedron-like. The compression affects the As--As intermolecular distances more than As--O separations, which at 30 GPa amount to 74% and 79% of the ambient-pressure values, respectively. The experimentally measured effects compare well with different quantum mechanical models. None of the calculations pointed to a phase transition either. It has been found that plane wave basis set and PBE functional augmented with the Grimme’s dispersion correction (PBE-D2) yield the best predictions and the application of the pob-TZVP Gaussian basis set leads to the overestimation of arsenolite bulk modulus. The computations of arsenolite band structure indicate that its band gap decreases from 4.2 eV at ambient pressure to 2.7 eV at 27.8 GPa. Last but not least, we have found very convincing experimental evidence of the formation of As2O2He inclusion compound whose crystal structure is proposed. To the best of our knowledge this is the first report on a noble gas inclusion compound in a host lattice of a molecular oxide.

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**Notes and references**